AD-A247 628

REPORT DOCUMENTATION PAGE

(2)

DTIC ELECTE MAR 19 1992 S D

1b RESTRICTIVE MARKINGS	
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION / AVAILABILITY OF REPORT: This document has been approved for public release and sale; its distribution is unlimited.
2b DECLASSIFICATION / DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S): 12	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION: NIST	6b OFFICE SYMBOL (If applicable)
7a. NAME OF MONITORING ORGANIZATION: ONR	
6c ADDRESS (City, State, and ZIP Code): A329, Materials Building, Gaithersburg, MD 20899	7b ADDRESS (City, State, and ZIP Code): Code 1131, 800 N. Quincy Street, Arlington, VA 22217-5000
8a. NAME OF FUNDING / SPONSORING ORGANIZATION: ONR	8b. OFFICE SYMBOL (If applicable)
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N00014-90-F-0011	
8c. ADDRESS (City, State, and ZIP Code)	10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT NO

11 TITLE (Include Security Classification)

12 PERSONAL AUTHOR(S): A. Feldman, E.N. Farabaugh, L.H. Robins, D. Shechtman

13a. TYPE OF REPORT	13b. TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Interim	FROM _____ TO _____	1992-Feb-20	19

16 SUPPLEMENTARY NOTATION

17 COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

This document has been approved for public release and sale: its distribution is unlimited.

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

CVD diamond, which is mainly polycrystalline, exhibits several materials problems that limit its optical transmission, such as scattering due to large surface roughness and absorption due to defects, nondiamond carbon phases, and impurities. Optical spectroscopy, Raman spectroscopy, cathodoluminescence imaging and spectroscopy, and high resolution electron microscopy are used to examine the defects in the material; however, a relationship between observed defects and optical abosrption is not always evident. New polishing methods are promising an abilitye to produce smooth surfaces in reasonable polishing times.

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified

22a NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

OFFICE OF NAVAL RESEARCH

Contract N00014-90-F-0011

R&T Project No. IRMT 025

TECHNICAL REPORT No. 12

DIAMOND AS AN OPTICAL MATERIALS

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submitted to

Characterization of Optical Materials

National Institute of Standards and Technology

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February 20, 1992

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DIAMOND AS AN OPTICAL MATERIAL(a,b)

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1. INTRODUCTION

The high transmissivity of perfect diamond over extensive regions of the electromagnetic spectrum, in combination with diamond's great hardness, large abrasion resistance, high thermal conductivity, and chemical inertness make diamond a highly desirable optical material. Until recently, the high cost and small dimensions of optical quality diamond have limited the use of diamond to a few specialized optical applications; the best optical quality diamond, type IIa diamond, still comes from natural sources. However, new chemical vapor deposition (CVD) processes have the potential to make available inexpensive bulk diamonds of large dimensions and thin film diamond to cover large areas, thus making possible the widespread use of diamond optics and optical coatings [1,2,3]. X-ray windows of CVD diamond are already commercially available [4]. Anticipated optical applications include infrared windows and domes, high power laser windows, and membranes for x-ray lithography [5]. Other possible applications include electroluminescent devices [6], lasers [7], and optical switches [8].

(b) This work was supported in part by the Office of Naval Research.
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This article focuses principally on the status of CVD diamond as an optically transparent material. CVD diamond, which is mainly polycrystalline, exhibits several materials problems that limit its optical transmission, such as scattering due to large surface roughness and absorption due to defects, nondiamond carbon phases, and impurities. New polishing methods have the potential for producing smooth surfaces in reasonable polishing times; however, work on surface figure, to our knowledge, has not yet been addressed. While intrinsic multiphonon processes limit the transmissivity of all diamond between 2.5 and 6.5 μm, CVD diamond usually contains high densities of lattice defects causing normally forbidden single phonon absorption processes to occur between 7.5 to 12 μm. In addition, free carrier absorption in CVD diamond has also been reported. While diamond windows less than 10 μm thick can be made transmissive to visible and ultraviolet radiation, thicker components scatter excessively and show absorption due to defects. Raman spectroscopy is the principal method for observing the presence of nondiamond carbon phases in CVD diamond.

An important method for examining point defects in CVD diamond is cathodoluminescence spectroscopy. When conducted in a scanning electron microscope (SEM), cathodoluminescence images can be generated that provide information about the spatial distribution of luminescent defects on a submicrometer scale. However, the relationship between the observed cathodoluminescence and defect induced optical absorption has not yet been established. Luminescence has been the basis for diamond devices that emit optical radiation. Lasers and electroluminescent devices have been made but the quantum efficiency at present is too small for these devices to be of practical use.

A powerful method for observing defects close to the atomic level is high resolution transmission electron microscopy. Here again, the relationship between observed defects and optical absorption has not be correlated.

Continuing research is improving the optical quality of CVD diamond. Recently, novel methods for producing single crystal (non-CVD methods) or near single crystal diamond have been reported. When fully developed, these methods could make available large optics of single crystal diamond.

High deposition temperature, large thermal expansion mismatch, and poor adhesion now limit the use of CVD diamond as a hard coating material. To overcome some of these difficulties, a method has been developed to place a diamond coating on ZnSe by bonding the coating to the substrate with a chalcogenide glass layer [9].

2. DISCUSSION

2.1 Deposition Methods

Several deposition methods are being used to deposit diamond by CVD. High quality polycrystalline diamond has been made by hot filament CVD [3], microwave plasma CVD [10], DC plasma torch [11], radio frequency plasma torch [12,13], microwave plasma torch [14], and oxyacetylene torch [15]. Figure 1 shows SEM images of diamond films showing typical surface

morphologies [16]. The morphologies observed are common to all of the deposition methods. The films were grown on silicon wafer substrates in a hot filament reactor under different deposition conditions.

Except for the oxyacetylene torch method, the charge gas for producing diamond is hydrogen mixed with a hydrocarbon such as methane, acetylene, methyl alcohol ethyl alcohol, or acetone [17]. The hydrogen fraction in the feed gas is almost always greater than 90 per cent. The quality of the diamond usually improves with increasing hydrogen fraction in the feed gas. It is also found that oxygen added to the charge gas improves the diamond quality [18]. Carbon monoxide mixed with hydrogen has also been used [19]. In the plasma torch methods, argon is sometimes used as a sheath gas. In the case of the oxyacetylene torch, only acetylene and oxygen comprise the charge gas. In this case, deposition is carried out in the reducing part of an oxygen-poor torch flame.

Substrate temperatures during deposition are usually maintained at a constant temperature in the range 600 to 1000 °C. Depositions have been done at temperatures below 400 °C [20]; however, the growth rates are low and the quality of the diamond, as determined by Raman spectroscopy, is poor. Recently, depositions by the oxyacetylene torch method at substrate temperatures up to 1600 °C have resulted in the growth of single crystal diamonds at high growth rates [21]. The method appears very promising for producing boule-sized single crystal diamonds of high optical quality.

A creative method for producing nearly single crystal diamonds layers over large areas has been developed recently [22]. Selective area etching was used to produce an array of etch pits of a well defined pyramidal shape in a single crystal silicon substrate. A slurry containing single crystal diamond particles of a matching pyramidal shape was applied to the surface of the substrate and then removed. Diamond particles that had been left behind were embedded in each of the etch pits. These particles were crystallographically oriented to within several degrees. When the substrate was placed in a CVD reactor, the diamond particles acted as seeds for diamond growth, resulting in a continuous diamond film that was nearly a single crystal.

There have been two reports of single crystal diamond nucleation on single crystal copper substrates. Both methods rely on the lack of solubility of carbon in copper. In one experiment [23], carbon ions were implanted into a single crystal copper substrate at an elevated temperature. A transmission electron microscope diffraction pattern indicated that a single crystal diamond layer had formed on the surface of the copper.

In the other experiment, carbon ions were implanted into single crystal copper substrates at room temperature [24]. The surface of the specimen was then exposed to high power radiation from an excimer laser. The laser pulse energy was chosen to cause the surface of the copper substrate to melt and then to refreeze rapidly. During refreezing of the copper, the carbon atoms were expelled and forced to the surface, precipitating on the surface as a diamond layer.

A halogen-assisted CVD method has recently been discovered for producing diamond [25]; however, this research is in an early stage and claims for

good quality diamond films made by this method have not yet been reported.

2.2 Optical Properties of CVD Diamond.

Many of the projected optical applications of CVD diamond are based on the known intrinsic properties of diamond. The intrinsic absorption mechanisms of diamond are due to interband transitions of electrons across the fundamental electronic energy gap at 5.45 eV, and to multiphonon generation in the infrared between 2.5 and 6.5 μm. Generally, absorption due to 2-phonon and 3- phonon generation predominates; higher order phonon generation has significantly decreased probability. Absorption due to generation of single phonons is forbidden because of crystal symmetry. Thus, perfect diamond is transparent between 225 nm in the ultraviolet and 2.5 μm in the infrared, and from 6.5 μm in the infrared to zero frequency (DC). Because the absorption process in the infrared between 2.5 and 6.5 μm is of second order and higher, the absorption coefficients are small so that thin diamond films may transmit adequately for many infrared applications in this wavelength range.

CVD diamond is not yet of the quality of the best natural single crystals because of the high density of defects in the material [26]. Several types of defects are present. Lattice defects, such as grain boundaries, twin boundaries, stacking faults, and dislocations, break the crystal symmetry of the diamond lattice resulting in absorption due to generation of single phonons. Thus, absorption by single phonon generation in CVD diamond has been observed at wavelengths longer than 6.5 μm. Many of the principal features in the diamond phonon spectrum have been identified in these transmission spectra [26].

Impurities can produce electronic states within the electronic band gap or can lead to local vibrational modes resulting in unwanted absorption. Nitrogen is known to significantly limit the transmission of diamond in the ultraviolet and is responsible for absorption features in the infrared [27]. Hydrogen in combination with carbon produces a C-H stretch absorption feature in the infrared near 2800 cm-1 [26,28-35]. Other spectral features due to hydrogen have been observed in bulk diamond and may be present in CVD diamond [36].

Figure 2 shows an infrared absorption spectrum of a CVD diamond polycrystalline specimen prepared by microwave plasma CVD showing the one phonon, two phonon, and three phonon absorption regions and absorption due to a C-H stretch mode [26].

CVD diamond usually contains nondiamond carbon phases that induce absorption, especially in the visible and ultraviolet. Figure 3 shows the absorption coefficient of CVD diamond and of type IIa diamond in the vicinity of the indirect absorption edge near 5.5 eV [37]. The higher absorption coefficient and the absorption tail extending to lower photon energies for the films is believed due to disordered carbon.

The presence of nondiamond phases of carbon is usually detected by Raman spectroscopy. The Raman spectrum of pure diamond consists of a single peak located at 1332 cm-1 wavenumber shift. CVD diamond usually exhibits an additional broad peak near 1500 cm-1 that is attributed to the nondiamond carbon phases. The sizes of the two peaks (after substraction for any

luminescence background signal) can be used as a qualitative measure of the diamond quality. Figure 4 shows a Raman spectrum typical of CVD diamond.

Recent experiments have shown that diamond can be made highly transmissive in the far infrared. Attenuation of the optical signal was attributed both to free carrier absorption and to optical scatter [35].

2.3 Defects in CVD Diamond

Defects such as nondiamond phases of carbon, point defects, impurities, lattice imperfections, etc., are an important factor in the optical performance of CVD diamond. Cathodoluminescence imaging and spectroscopy provide a means for examining point defects and impurities in diamond on a microscopic scale [38]. In this method, the specimen is placed in a scanning electron microscope and the optical radiation emitted by the specimen is collected by a photodetector. The optical signal arises when valence band electrons are excited above the fundamental energy gap of the diamond into the conduction band by the energetic electron beam (>10 kV) of the SEM. The electrons in the conduction band can decay to defect states within the band gap. The electrons may lose energy from these defect states by emitting optical radiation whose spectral features are characteristic of the defect center.

The cathodoluminescence provides an optical image of the specimen as the electron beam scans over the specimen. This image can be compared to the secondary electron image customary observed with the SEM. Figure 5 shows a cathodoluminescence image and a secondary electron SEM image of diamond particles deposited by CVD. The cathodoluminescence image provides information regarding the distribution of luminescent defects in the diamond. However, the interpretation of the image in terms of defect densities is not necessarily straightforward because the intensity of the luminescence from a particular defect species depends not only on the number density of that species but also on the densities of other species that give rise to competing decay processes.

By a spectral analysis of the cathodoluminescence, one can deduce the nature of the defect centers. This identification is based on a large body of work in which the luminescence spectra of many defects have been identified. Figure 6 is the cathodoluminescence spectrum of a diamond film that shows several spectral features often observed in CVD diamond. These features have been associated with particular defects: a sharp line at 1.68 eV believed to be due to a silicon impurity introduced during deposition (this feature is identical to the luminescence line frequently observed at 5890 cm-1 in the Raman spectrum); a line at 2.156 eV and an associated vibronic band centered near 2 eV, due to a nitrogen-vacancy (N-V) complex; a line at 2.326 eV due to a different N-V complex; and, a broad violet band centered at 2.85 eV, due to a dislocation related defect. A line at 3.188 eV due to a nitrogen interstitial-carbon complex has also been observed in some CVD diamond films.

High resolution electron microscopy is a powerful tool for examining defects in CVD diamond at the lattice scale [39]. Figure 7 shows a high resolution electron micrograph of CVD diamond with a <110> orientation showing a large number of twinning defects. The film was prepared by the microwave plasma technique and thinned for examination in the electron microscope. All

of the observed twins retain a crystallographical relationship to each other. All arrows point to misfit twin boundaries, which are described below. The hollow arrows also point along local growth directions.

A preferred nucleation site for diamond growth is a location where five twins come together to a point. This structure is called a twin quintuplet. Figure 8 is an enlarged view of a twin quintuplet and several other twins. A coherent twin boundary occurs when {111} planes of adjacent twins are in coincidence and this is evident for most of the twin boundaries in the figure.

Because the angle between {111} planes in a crystal twin is 70.5°, a 7.5° angular mismatch occurs at one of the boundaries in a twin quintuplet; this twin boundary is not coherent and is called a misfit boundary. In the figure, the arrow marked A points to the beginning of a misfit twin boundary that meanders toward the periphery of the crystal. A misfit boundary can terminate within the crystallite or it can extend to the crystallite surface. Because the misfit boundary is the surface at which the crystal growth terminates locally, the local growth direction points along the boundary away from the nucleation site.

2.4 Polishing CVD Diamond

CVD diamond films usually grow with surfaces that are undesirable for most optical application because of a large surface roughness. Smooth diamond films can be made if the nucleation density is high; however, the thickness of such films is limited to several micrometers as the roughness tends to increase with increasing film thickness. However, in a recent paper, Wild et al. [40] have reported that diamond films grown with a <100> texture appear to grow smoother as the film thickness increases. Films of this type have been grown to thicknesses greater than 100 μm. Transmittance measurements indicate that these films show a higher optical transmittance that conventionally grown CVD diamond films.

Methods of polishing CVD diamond films are being developed to produce smooth films. Because CVD diamond is polycrystalline and hard, it is very difficult to polish; polishing by conventional methods is very slow. Wang et al. [33] have polished CVD diamond films on a cast iron scaife heated to 350 °C. Six weeks of polishing were required to obtain a mirror-like surface. To increase the polishing rate, a sample was annealed in an atmosphere of 0.01% oxygen in argon at 1000 °C for 4 hours; the film surface turned black. In this case, the time for polishing was reduced to one week. Polishing with potassium nitrate also increased the polishing rate; however, the specimen had to be carefully monitored to avoid destruction. Polishing decreased the peak-to-valley surface roughness from 1.2 μm to less than 0.1 μm.

Yoshikawa [41] has pioneered a thermochemical method for polishing diamond at high rates. In his method, a rotating polishing plate of iron (of low carbon content) or nickel is held at an elevated temperature inside an environmental chamber capable of supporting a vacuum. The CVD diamond surface is polished by holding it in contact with the rotating plate. In an atmosphere of hydrogen, iron produced the highest polishing rate and nickel produced nearly as high a polishing rate. No polishing action was observed with molybdenum plates or with cast iron plates and no polishing was observed at 700 °C or lower. At 750 °C and above, the polishing rate increased with

increasing temperature. At 950 °C, the entire surface was polished after 20 min. The polishing rate also increased with applied pressure; however, excessively high pressures made the polishing process unstable. Increasing the lapping speed also increased the polishing rate. The average roughness, Ra, obtained on a 7 mm square specimen was 2.7 nm.

Frequently, the diamond surface is too rough for polishing directly. Yoshikawa has planed the surface of the specimen prior to polishing by irradiating the specimen with a Q-switched Nd-doped yttrium aluminum garnet (Nd:YAG) laser in one atmosphere of oxygen. A peak-to-valley roughness of 3 μm could be obtained by this process. Several authors have used variations of Yoshikawa's method to polish CVD diamond [42,43]

Protrusions that sometimes grow on the diamond surface must be removed prior to polishing. Harker et al. [42] have used reactive plasma etching to remove such protrusions. In order to etch only the protrusions and not the surrounding material, a nonreactive gold coating was applied to the entire surface. The protrusions were then exposed for reactive plasma etching with oxygen.

Another method of polishing CVD diamond by ion beam polishing has been developed [44]. The rough surface of a diamond specimen is spin coated with a mixture of photoresist and a Ti-silica emulsion to produce a plane surface. The surface is then etched with an oxygen ion beam; the angle of incidence is chosen to match the etching rate of the coating with the etching rate of diamond. The average root-mean-squared roughness on a 5 cm diameter film was 4.9 nm.

2.5 X-ray Window

Because of its low atomic number, carbon is highly transparent to x-ray radiation. The excellent mechanical properties of diamond make it useful as an ultrathin x-ray window for an energy dispersive x-ray fluorescence detector [4]. This has been the first practical use of CVD diamond for tranmitting electromagnetic radiation. In this application, diamond is replacing beryllium which must be made considerably thicker to support a vacuum. The optical transparency and mechanical stability of diamond also make CVD diamond a possible membrane material for x-ray masks. X-ray masks are used in the x-ray lithography of integrated circuits [5].

3. CONCLUSION

The superior properties of diamond make it a candidate for a number of optical applications. The most immediate application is the diamond x-ray window. The quality of CVD diamond for other applications, such as infrared transmissive elements and coatings, is continually improving but is not yet sufficient. Surface roughness is a major impediment to optical applications. The ability to deposit smooth surfaces would make diamond considerably more attractive as an optical material. Polishing is being pursued as a means for making smooth CVD diamond surfaces. Diamond also has promise as a blue luminescent or laser material. Identifying and controlling the relevant luminescent defect centers will be needed to improve the quantum efficiencies of such devices.

4. ACKNOWLEDGEMENT

We thank J.L. Hutchison of Oxford University for his assistance in obtaining the high resolution electron micrographs.

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Figure Captions

Figure 1. SEM images of diamond film surfaces exhibiting a range of morphologies. All of the films were grown at from a hydrogen-methane mixture in a hot filament CVD reactor: (upper left) "cauliflower" morphology; (upper right) {110} morphology; (lower left) triangular {111} morphology; (lower right) {100} morphology.

Figure 2. Infrared absorptance spectrum of a CVD diamond specimen prepared by microwave plasma CVD, courtesy of C. Klein of the Raytheon Company [26].

Figure 3. Absorption coefficients of CVD diamond films and type IIa diamond in the vicinity of the absorption edge.

Figure 4. Raman spectrum typical of CVD diamond showing a sharp diamond peak a 1332 cm-1 and a broad diamondlike carbon peak around 1500 cm-1.

Figure 5. Cathodoluminescence image of diamond particles (left) and the corresponding SEM image (right).

Figure 6. Cathodoluminescence spectrum of CVD diamond film showing principal spectral features.

Figure 7. High resolution electron micrograph of CVD diamond with a <110> orientation. The arrows point to misfit twin boundaries, surfaces where twins grow together noncoherently. The hollow arrows indicate local growth directions.

Figure 8. High resolution electron micrograph showing a twin quintuplet. The arrow is pointing to the start of a misfit boundary. A misfit boundary is a surface where two twins grow together noncoherently. The arrow also points in a direction of local growth.

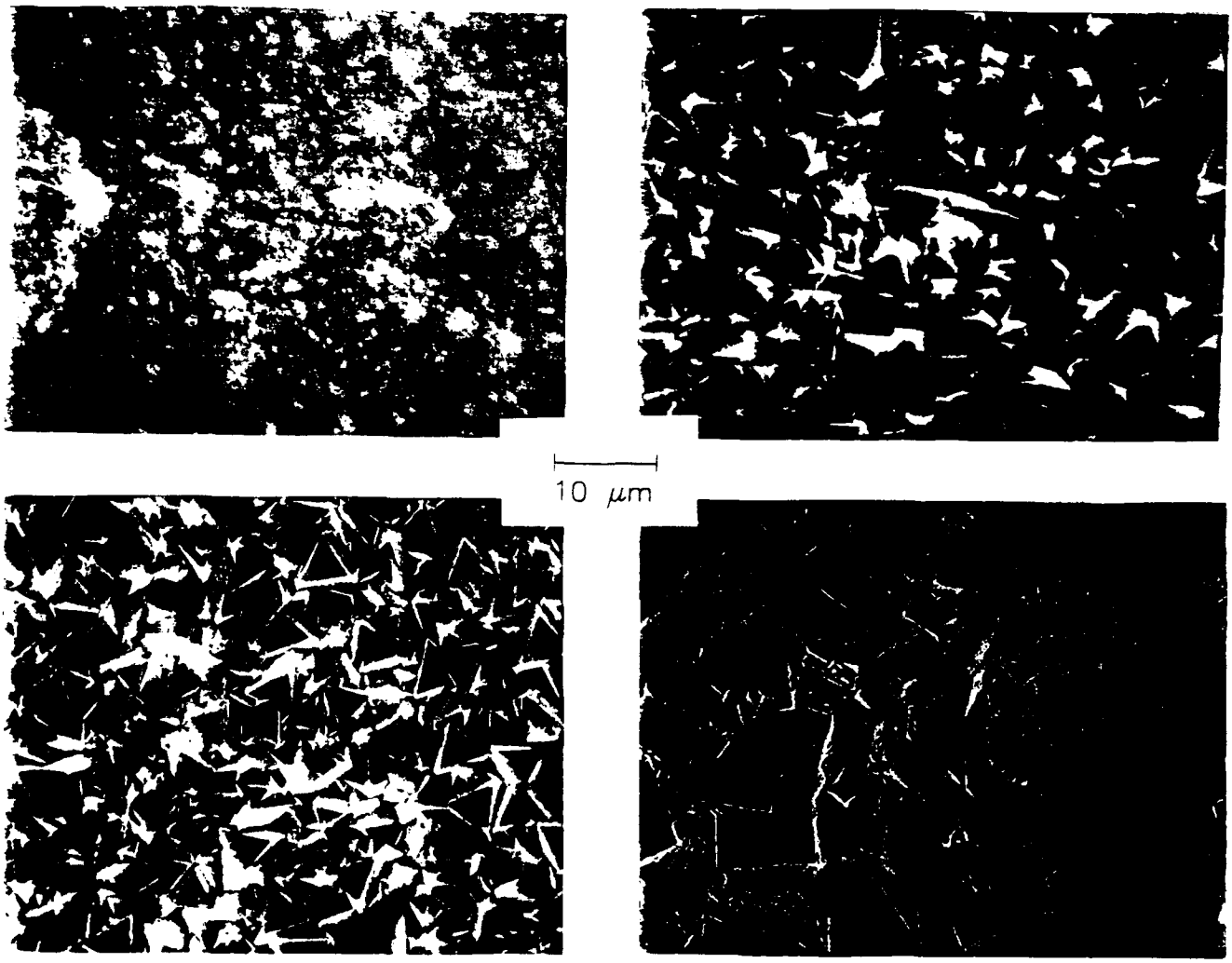


Figure 1. SEM images of diamond film surfaces exhibiting a range of morphologies. All of the films were grown at from a hydrogen-methane mixture in a hot filament CVD reactor: (upper left) "cauliflower" morphology; (upper right) {110} morphology; (lower left) triangular {111} morphology; (lower right) {100} morphology.

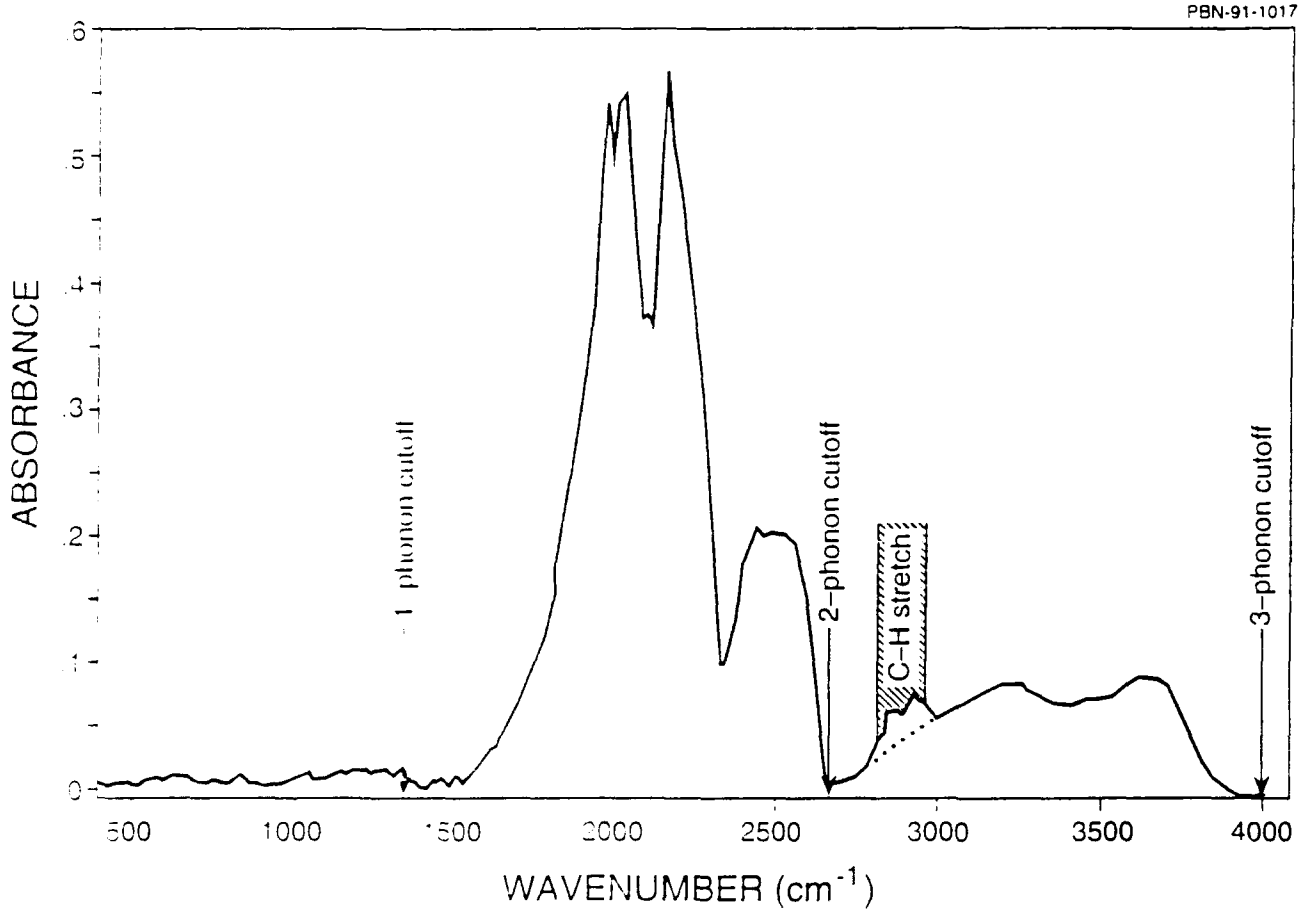


Figure 2. Infrared absorptance spectrum of a CVD diamond specimen prepared by microwave plasma CVD, courtesy of C. Klein of the Raytheon Company [26].

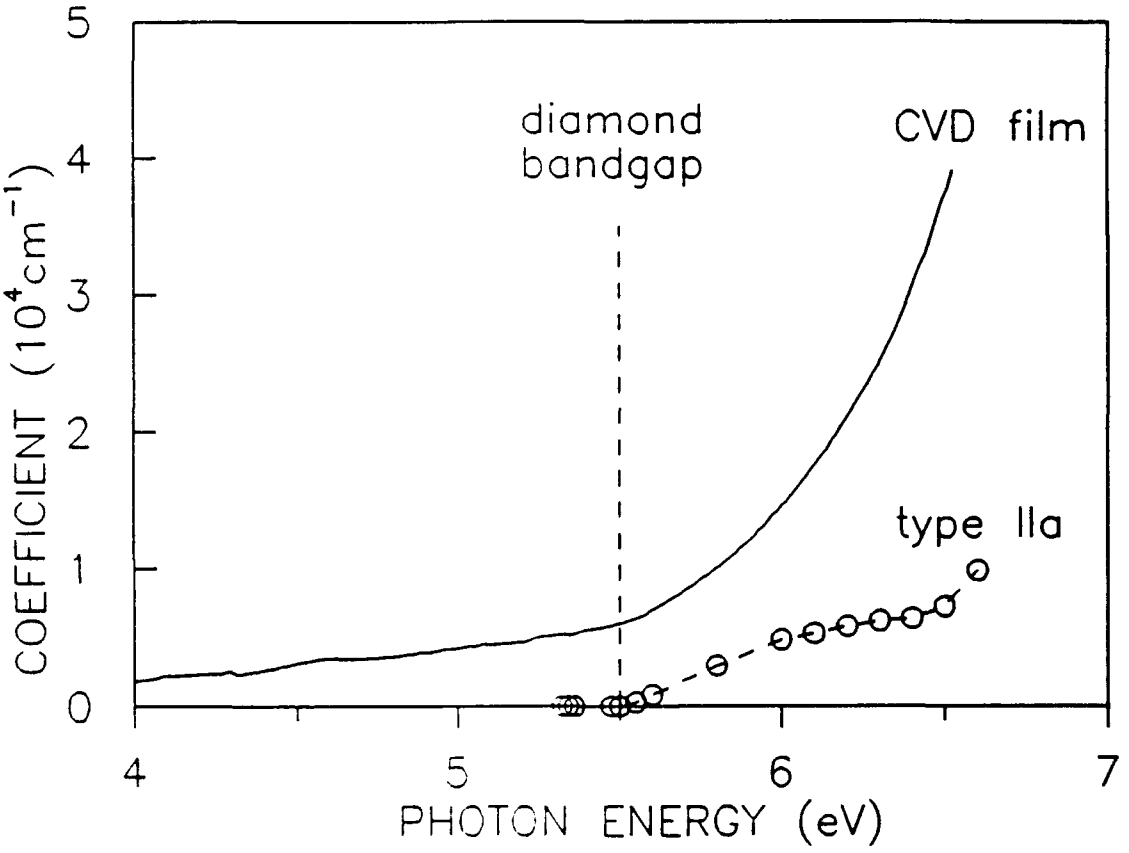


Figure 3. Absorption coefficients of a CVD diamond film and a type IIa diamond in the vicinity of the absorption edge.

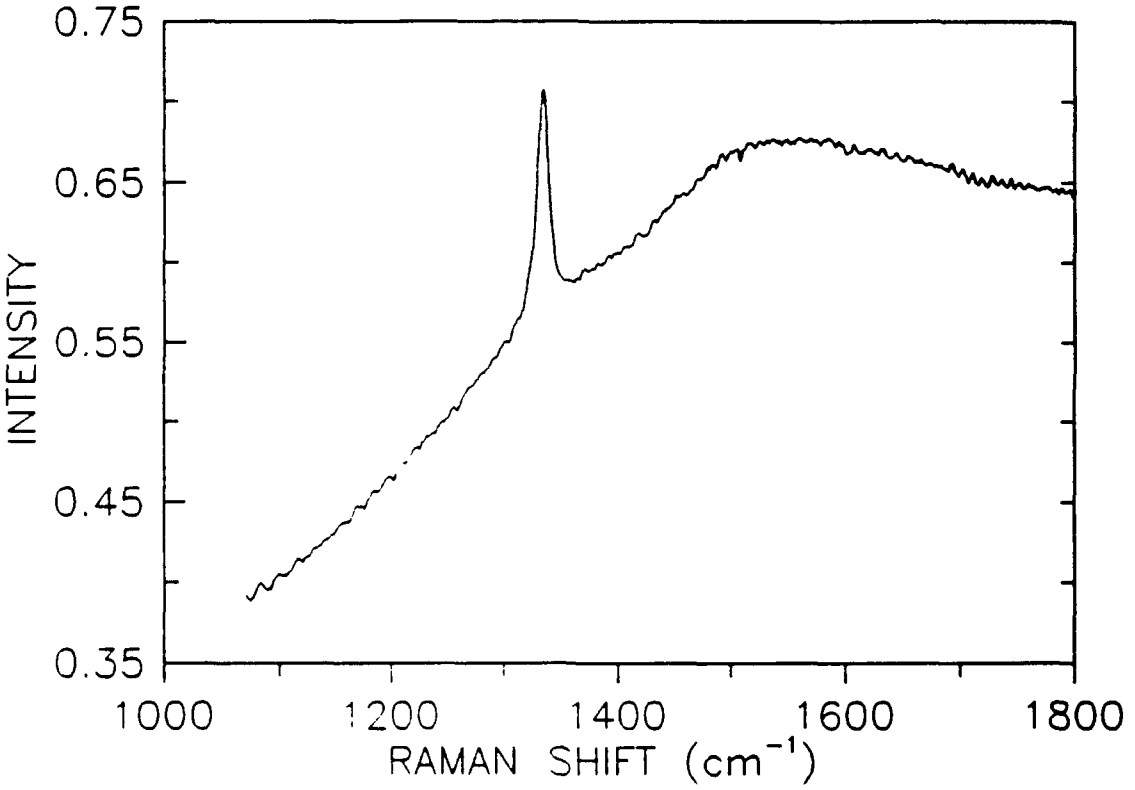
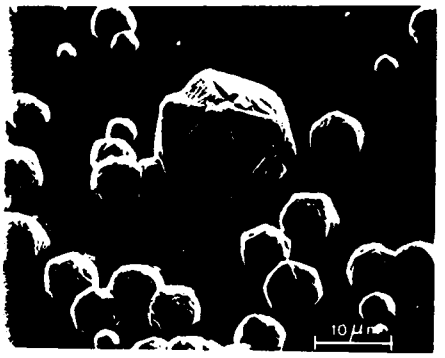


Figure 4. Raman spectrum typical of CVD diamond showing a sharp diamond peak a 1332 cm-1 and a broad diamondlike carbon peak around 1500 cm-1.

CL IMAGE



SECONDARY-ELECTRON IMAGE

Figure 5. Cathodoluminescence image of diamond particles (top) and the corresponding SEM image (bottom).

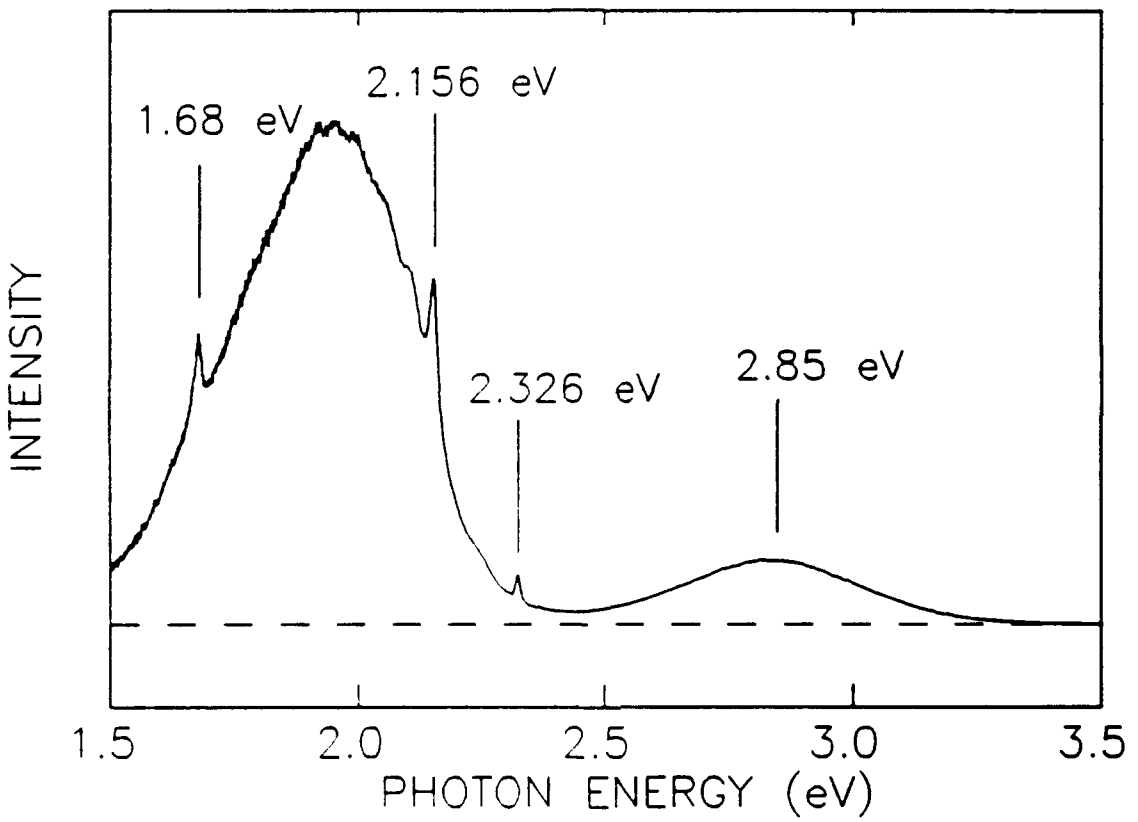
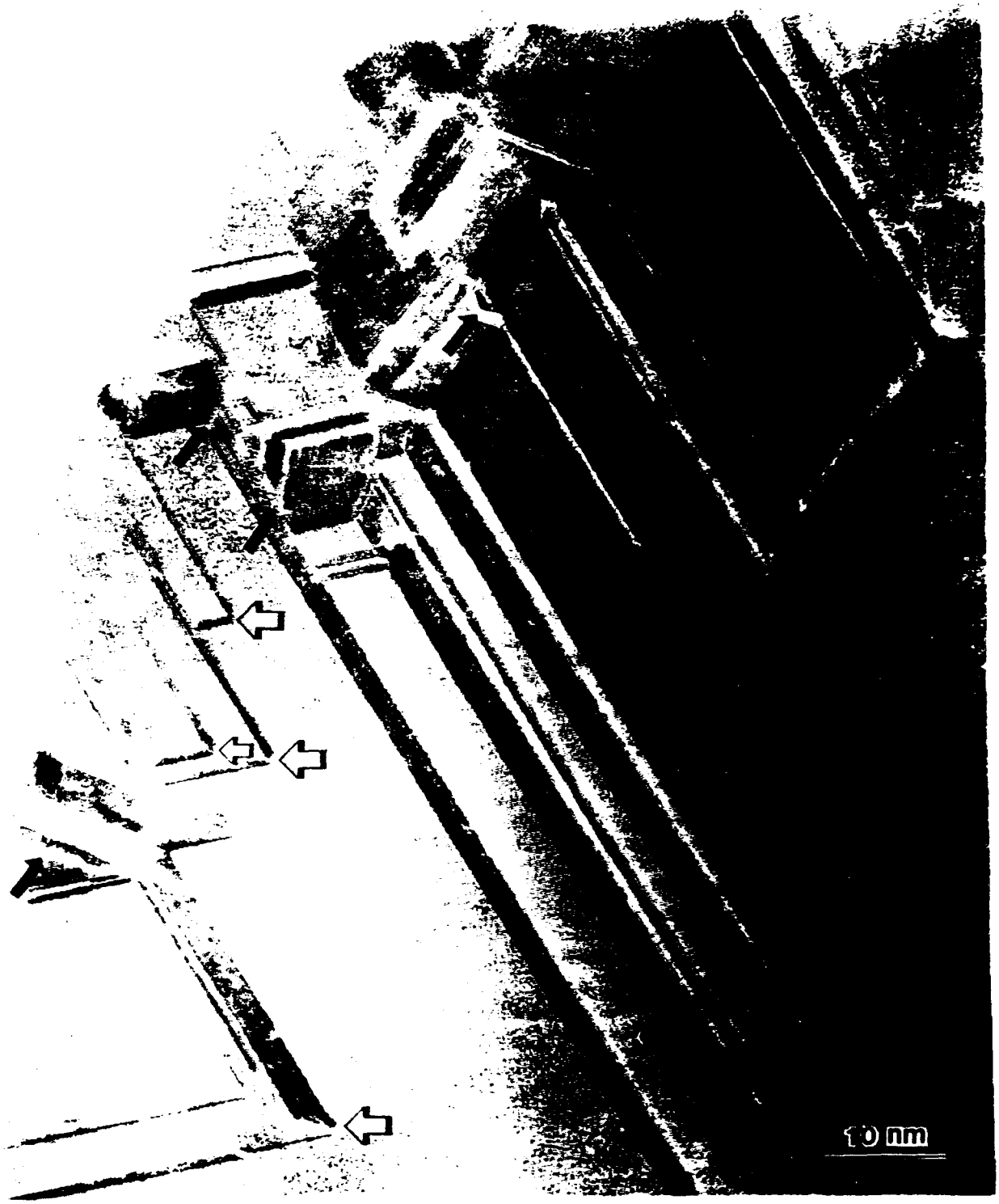


Figure 6. Cathodoluminescence spectrum of CVD diamond film showing principal spectral features.



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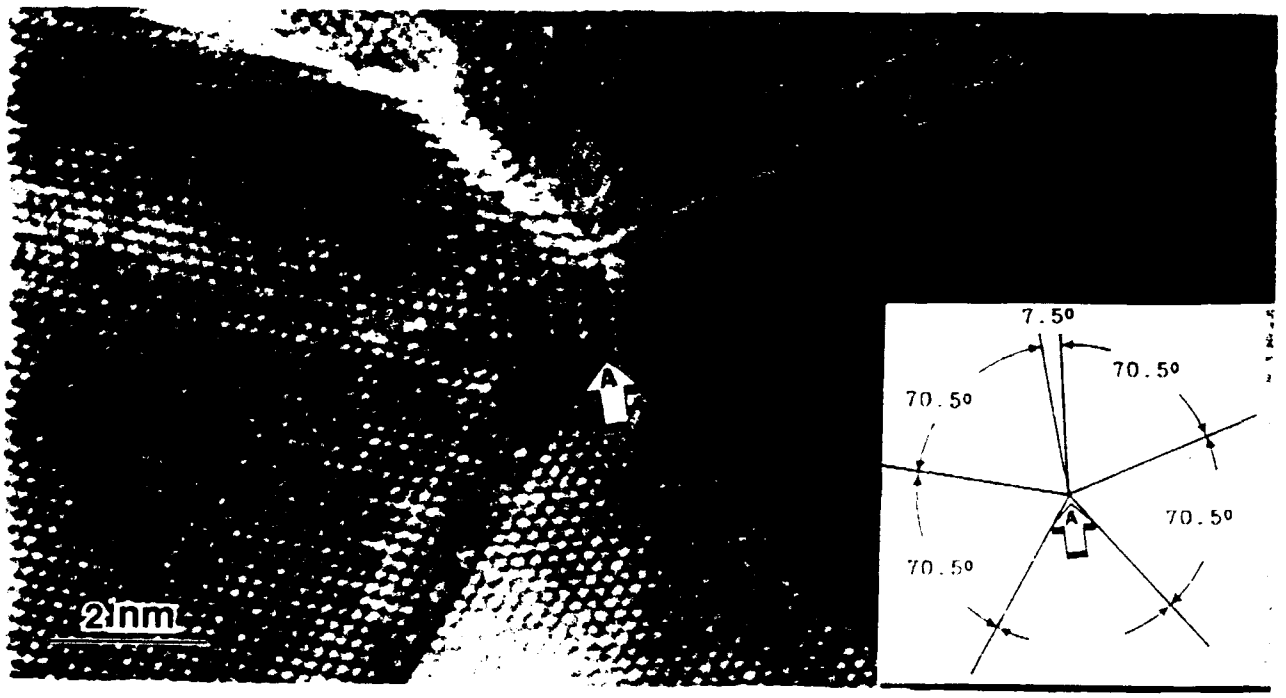

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